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The "corset effect" of spin-lattice relaxation in polymer melts confined in nanoporous media

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Abstract

Linear polyethylene oxides with molecular weights Mw of 1665 and 10170 confined in pores with variable diameters in a solid methacrylate matrix were studied by proton field-cycling nuclear magnetic resonance relaxometry. The pore diameter was varied in the range of 9-57 nm. In all cases, the spin-lattice relaxation time shows a frequency dependence close to T1 ∝ ν3/4 in the range of ν = 3·10 -1-2·101 MHz as predicted by the tube-reptation model. This proton T1 dispersion essentially reproduces that found in a previous deuteron study (R. Kimmich, R.-O. Seitter, U. Beginn, M. Möller, N. Fatkullin: Chem. Phys. Lett. 307, 147, 1999). As a feature particularly characteristic for reptation, this finding suggests that reptation is the dominating chain dynamics mechanism under pore confinement in the corresponding time range. The absolute values of the spin-lattice relaxation times indicate that the diameter of the effective tubes in which reptation occurs is much smaller than the pore diameters on the time scale of spin-lattice relaxation experiments. An estimation leads to a value d* ~ 0.5 nm. The impenetrability of the solid pore walls, the uncrossability of polymer chains (·excluded volume·) and the low value of the compressibility in polymer melts create the ·corset effect· which reduces the lateral motions of polymer chains to a microscopic scale of only a few tenths of a nanometer.